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[54] Patent Name: A synthetic method for an AB type block copolymer and the AB type block copolymer prepared by this method

[57] Abstract:
This invention involves a synthetic method for an AB type block copolymer and the AB type block copolymer prepared by this method, the A block in this copolymer is polyvinyl acetate, B block is a polymer of polystyrene and poly (methyl) acrylic acid (acrylate). The procedure is to first form a prepolymer of polyvinyl acetate by vinyl acetate under the existence of carbon tetrachloride and initiator, and then the prepolymer reacts with vinyl monomer under the existence of catalyst to form the AB type block copolymer in this invention. Its molecular weight distribution index is low, the structure is clear; therefore it is a block copolymer with wide application future.

PATENT CLAIMS

1. A synthetic method for an AB type block copolymer and the AB type block copolymer prepared by this method, the feature is that: vinyl acetate (VAc), carbon tetrachloride and radical initiator are placed in a reactor, a prepolymer is formed after the reaction, then the prepolymer, catalyst and vinyl monomer (M) are placed inside the reactor to form the AB type block copolymer in this invention inside a nitrogen or argon environment.

2. The method of claim 1 wherein the feature is that the above radical initiator is an azo type radical initiator.

3. The method of claim 1 wherein the feature is that the structural characteristic of the prepolymer is a linear polyvinyl acetate, there are two end groups, one is methyl trichloride, the other one is nitrogen substitute, its structure is Cl-(VAc-)-$_n$$CCl_3$.

4. The method of claim 1 wherein the feature is that the synthesis temperature for the prepolymer is 30~110°C.

5. The method of claim 1 wherein the feature is that the applied catalyst can be coordination compounds formed by CuCl, CuBr and 2,2'-dipyridyl and its alkyl substitutes.

6. The method of claim 1 wherein the feature is that the applied vinyl monomer can be styrene, (methyl) acrylic acid (acrylate).

7. The method of claim 1 wherein the feature is that the reaction temperature after catalyst, monomer and solvent are added is 30~140°C.

8. The method of claim 1 wherein the feature is that the synthesized AB type block copolymer has the following structural character tics: (a) inside the AB type block copolymer, the point that connects A and B blocks is a saturated carbon atom that contains two chlorine atoms, it has one chlorine atom at each end, the structure is Cl-(-VAc-)-$_n$$CCl_2$-(-M-)-$_m$Cl; (b) the A block of the AB type block copolymer is polyvinyl acetate, the molecular weight of A block is 1000~60000; (c) the B block of the AB type block copolymer is polystyrene, poly (methyl) acrylic acid (acrylate), the molecular weight is 500~90000; (d) the molecular weight of the AB type block copolymer is 2000~150000.

A Synthetic Method for an AB Type Block Copolymer and the AB Type Block Copolymer Prepared by the Method

This invention involves a high polymer synthetic method for an AB type block copolymer, this AB type block copolymer is a diblock copolymer composed of polyvinyl acetate and other polymers containing vinyl monomers.

It is well known that the high molecular homopolymers and copolymers polymerized by small molecular monomers have been widely used in plastics, rubber, chemical fiber, coating, polymer assistant and other high molecular fields. Because AB type block copolymer contains two chain structures with different properties at the same time, it displays characteristics that are different from A and B, the applicable range of the product is greatly expanded. The diblock copolymer formed by polyvinyl acetate and other monomers is one type of polymers that attracts researchers' attention; its current synthetic methods are listed below:

1. Article Liu, Futian; Cao, Shuqin, J. Appl. Polym. Sci. 48(3), 425-434 (1993) reported a low polymer of polystyrene containing sulfhydryl groups obtained through the telomerization of styrene and other monomers under the existence of sulphur containing compounds, then this polymer is used in the telomerization of vinyl acetate to obtain polystyrene-polyvinyl acetate diblock copolymer containing sulphur. There are many side reactions in this method and the system is complicated.

2. Japanese Patent JP 01,174,513 reported a peroxide initiator. Under two different temperatures, it can initiate different monomers to synthesize diblock copolymer composed of polyvinyl acetate and other vinyl monomer polymer compositions. The two blocks in this block copolymer are connected by the initiator pieces, the two end groups are undetermined, and this method also has the shortcomings such as: many side reactions, complicated composition and wide molecular weight distribution.

3. Article Mardare, Deniela, Malyjaszewski, Krzysztof, Polym. Prep. 34 (2), 566-7(1993) reported a method to synthesize polyvinyl acetate block copolymer using aluminum alkyl as catalyst, the two end groups of the synthesized block copolymer are non-chlorine substitute groups, the connection of the two blocks is a random copolymer chain. This system is very complicated, there are many side reactions and the used reagents are easily flammable and can explode.

4. Article M. Destarac, J.M. Bessiere, Bouteven, polym. preprins. 38(1), 677-8(1997) mentioned a redox telomerization reaction, it can synthesize vinyl acetate – styrene block copolymer, but the molecular weight of the A block in this AB type block copolymer is less than 700, and it does not contain chlorine atom, there is no clear molecular weight and molecular weight distribution data.

The purpose of this invention is to overcome the shortcomings of the current technologies, and provide a new method for AB type diblock copolymer containing polyvinyl acetate, wherein A block is polyvinyl acetate and B block is polystyrene or poly (methyl) acrylic acid (acrylate). This method has mild reaction condition, the applicable monomer range is high, the structure of the obtain polymer is clear, the lengths and ratio of A and B blocks are adjustable; the molecular weight distribution is narrow.

The thoughts behind this invention are listed below:

Vinyl acetate, carbon tetrachloride, radical initiator and solvents are placed in the reactor, a prepolymer with methyl trichloride on one end and one chlorine atom on the other end is produced after the reaction, the prepolymer initiates the monomer polymerization of styrene or (methyl) acrylic acid (acrylate) under the existence of catalyst to obtain an AB type block copolymer with one chlorine atom at each end, the connecting point for A and B is a saturated carbon atom with two chlorine atoms.

The thoughts behind this invention can also be realized this way:

Vinyl acetate, carbon tetrachloride, radical initiator, solvent 1 (solvent is not required) are placed in the reactor, the obtained material is dissolved by solvent 1, and precipitated by precipitating agent 1, after many treatments, the obtained material is precipitated and dried to obtain a prepolymer, the prepolymer, catalyst, vinyl monomer, solvent 2 (solvent is not required) are placed in the reactor to react, the obtained material is dissolved by solvent 2, and precipitated by precipitating agent 2, after many treatments, it is precipitated and dried to obtain an AB type block copolymer with one chlorine atom at each end, the connecting point for A and B is a saturated carbon atom with two chlorine atoms.

The above solvent 1 can be methanol, ethyl alcohol, butyl alcohol, acetone, butyl ketone, acetate, tetrahydrogen furan, dioxane, benzene and its alkyl substitutes.

The above precipitating agent 1 can be water, petroleum ether or their mixture with solvent 1.

The above catalyst can be CuCl, CuBr and coordination compounds between dipyridyl or its alkyl substitutes.

The above solvent 2 can be benzene and its alkyl substitutes, tetrahydrogen furan, dioxane, diphenyl ether, phenyl methyl ether, acetate, acetone, butyl ketone, N,N-dimethyl formamide.

The above precipitating agent 2 can be methanol, ethyl alcohol, glycerol, water, methanol/water, ethyl alcohol/water, glycerol/water, petroleum ether or their mixtures with solvent 2.

The molecular weight of the above prepolymer is 1000~60000, one end of the prepolymer contains a chlorine atom, the other end contains methyl trichloride, the structure is Cl-(-VAc-)$_n$-CCl_3. VAc represents vinyl acetate.

The above vinyl monomer can be styrene, (methyl) acrylic acid (acrylate).

The A block of the above AB type block copolymer is polyvinyl acetate, the molecular weight is 1000~60000; B block is a polymer formed by styrene and (methyl) acrylic acid (acrylate), the molecular weight of B block is 500~90000; the molecular weight of the AB type block copolymer is 2000~150000; the connecting point of A and B is a saturated carbon atom containing two chlorine atoms, there is one chlorine atom at each end, the structural formula is: Cl-(-VAc-)$_n$-CCl_2-(-M-)$_m$-Cl, M represents styrene or (methyl) acrylic acid (acrylate).

The synthetic processing conditions for the AB type block copolymer are listed below:

Vinyl acetate monomer, carbon tetrachloride, solvent 1 and radical initiator are placed in the reactor, nitrogen or argon is used to exchange the air in the system. The mixture is stirred under 30~110°C and reacted for over 0.5 hour (generally is 1~10 hours), after the temperature is reduced, the material is dissolved by solvent 1, and precipitated by precipitating agent 1, after many treatments, the material is dried to receive a prepolymer, it goes into the reactor with catalyst, vinyl monomer, solvent 2 (solvent is not required), the mixture is stirred under 30~140°C and reacted for over 0.5 hour (generally is 2~48 hours), the material is then dissolved by solvent 2, and precipitated by precipitating agent 2, after many treatments, the material is dried to receive the AB type block copolymer in this invention.

The synthesis of diblock copolymer containing polyvinyl acetate is difficult, especially obtaining the AB type block copolymer with the above structure is even more difficult, among the current synthesis methods, whether organic material containing sulphur is used in telomerization process, or bifunctional peroxide is used to initiate the polymerization between two monomers under different temperature, they both inevitably cause many side reactions, the molecular weight of the block copolymer is hard to control, the operation is complex, the aluminum alkyl system is complicated and aluminum alkyl is easily flammable and can explode, for the AB type block copolymer obtained by this method, the connection between A and B is not clear, the molecular weight of the AB type block copolymer is low, the molecular weight for A block in the AB type block copolymer synthesized by redox telomerization is too small, there is no clear molecular weight and molecular weight distribution data for the AB type block copolymer. For the AB type block copolymer obtained in this invention, the A and B blocks are only connected by one carbon atom containing chlorine atoms, there is one chlorine atom that can be converted to other functional group at each end, the molecular weight of A block is higher, therefore it has higher percentage in the AB type block copolymer, it can fully represent the property of polyvinyl acetate. There are many applicable monomers for this invention, the structure of the obtained block copolymer is clear; the molecular weights

of A block, B block and AB can be adjusted based on needs. Therefore, using this invention, we can synthesize a very useful AB type polyvinyl acetate block copolymer that is difficult to obtain through other methods, the reaction condition is mild, the reagents can be easily obtained, the operational method is simple and easy to be industrialized.

Implementation Example 1

Inside a reaction bottle equipped with condenser, agitator, and nitrogen pipe, 45ml refined VAc monomer is added with 2ml carbon tetrachloride and 0.0747g AIBN, nitrogen is sent into the bottle to exchange air for 15 minutes, after agitation, the temperature is raised to 60°C, the reaction proceeds for 120 minutes while the temperature is maintained, then the mixture is cooled to room temperature, 40ml methanol is added, after agitation, the mixture is slowly poured into 200ml water, after precipitation, the material is washed by water, the treatment is repeated for 3 times, 34g of prepolymer is obtained after being dried for 8 hours at 50°C vacuum condition. GPC gel chromatography is used to obtain Mn=3088. Measure 1.000g of prepolymer, 0.0449g of cuprous chloride and 1.669g of 2,2-dipyridyl in the reactor, 5ml methyl butyl acetate and 5ml butyl acetate are injected by an injector, the prepolymer is fully dissolved after agitation, nitrogen is used to vacuum the reactor at -20°C for 3 times, the reactor is sealed, and the reaction proceeds for 24 hours at 125°C, the product is dissolved by tetrahydrogen furan and precipitated for 3 times with methanol, the precipitated material is dried for 2 hours at 50°C, than dried for 8 hours under 50°C vacuum condition to obtain 4.91g of prepolymer, the conversion rate is 87%. UR-IR analysis proves that it contains vinyl acetate and butyl methacrylate blocks, therefore the product is PVAc-b-PBMA block copolymer, GPC gel chromatography is used to obtain Mn=18042, the molecular weight distribution coefficient Mw/Mn=1.27.

Implementation Example 2

Inside a reaction bottle equipped with condenser, agitator, and nitrogen pipe, 45ml refined VAc monomer is added with 2ml carbon tetrachloride and 0.0747g AIBN, nitrogen is sent into the bottle to exchange air for 15 minutes, after agitation, the temperature is raised to 60°C, the reaction proceeds for 120 minutes while the temperature is maintained, then the mixture is cooled to room temperature, 40ml methanol is added, after agitation, the mixture is slowly poured into 200ml water, after precipitation, the material is washed by water, the treatment is repeated for 3 times, 34g of prepolymer is obtained after first being dried for 2 hours under 50°C and then being dried for 8 hours at 50°C vacuum condition. GPC gel chromatography is used to obtain Mn=3088. Measure 1.006g of prepolymer, 0.0420g of cuprous chloride and 0.1675g of 2,2-dipyridyl in the reactor, 5ml methyl methacrylate and 5ml dimethyl benzene are injected by an injector, the prepolymer is fully dissolved after agitation, nitrogen is used for 3 times to vacuum the reactor at -20°C, the reactor is sealed, and the reaction proceeds for 24 hours at 130°C, the product is dissolved by tetrahydrogen furan and precipitated for 3 times with methanol, the precipitated material is dried for 2 hours at 50°C, than dried for 8 hours under 50°C vacuum condition to obtain 5.020g of prepolymer, the

conversion rate is 89.3%. UR-IR analysis proves that it contains vinyl acetate and methyl methacrylate blocks, therefore the product is PVAc-b-PMMA block copolymer, GPC gel chromatography is used to obtain Mn=16801, the molecular weight distribution coefficient Mw/Mn=1.27.

Implementation Example 3

Inside a reaction bottle equipped with condenser, agitator, and nitrogen pipe, 45ml refined VAc monomer is added with 5ml carbon tetrachloride and 0.0500g AIBN, nitrogen is sent into the bottle to exchange air for 15 minutes, after agitation, the temperature is raised to 60°C, the reaction proceeds for 120 minutes while the temperature is maintained, then the mixture is cooled to room temperature, 40ml methanol is added, after agitation, the mixture is slowly poured into 200ml water, after precipitation, the material is washed by water, the treatment is repeated for 3 times, 31g of prepolymer is obtained after being dried for 8 hours at 50°C vacuum condition. GPC gel chromatography is used to obtain Mn=1243. Measure 0.2013g of prepolymer, 0.0153g of cuprous chloride and 0.0647g of 2,2-dipyridyl in the reactor, 3ml styrene monomer and 5ml diphenyl ether are injected by an injector, the prepolymer is fully dissolved after agitation, nitrogen is used for 3 times to vacuum the reactor at -20°C, the reactor is sealed, and the reaction proceeds for 24 hours at 120°C, the product is dissolved by tetrahydrogen furan and precipitated for 3 times with methanol, the precipitated material is dried for 2 hours at 50°C, than dried for 8 hours under 50°C vacuum condition to obtain 1.16g of prepolymer, the conversion rate is 66%. UR-IR analysis proves that it contains vinyl acetate and styrene blocks, therefore the product is PVAc-b-PSt block copolymer, GPC gel chromatography is used to obtain Mn=7014, the molecular weight distribution coefficient Mw/Mn=1.23.

Implementation Example 4

Inside a reaction bottle equipped with condenser, agitator, and nitrogen pipe, 45ml refined VAc monomer is added with 5ml carbon tetrachloride and 0.0500g AIBN, N_2 is sent into the bottle to exchange air for 15 minutes, after agitation, the temperature is raised to 60°C, the reaction proceeds for 120 minutes while the temperature is maintained, then the mixture is cooled to room temperature, 40ml methanol is added, after agitation, the mixture is slowly poured into 200ml water, after precipitation, the material is washed by water, the treatment is repeated for 3 times, 31g of prepolymer is obtained after being dried for 8 hours at 50°C vacuum condition. GPC gel chromatography is used to obtain Mn=1243. Measure 0.2300g of prepolymer, 0.0164g of cuprous chloride and 0.0666g of 2,2-dipyridyl in the reactor, 3ml methyl methacrylate and 3ml dimethyl benzene are injected by an injector, the prepolymer is fully dissolved after agitation, nitrogen is used for 3 times to vacuum the reactor at -20°C, the reactor is sealed, and the reaction proceeds for 24 hours at 130°C, the product is dissolved by tetrahydrogen furan and precipitated for 3 times with methanol, the precipitated material is dried for 2 hours at 50°C, than dried for 8 hours under 50°C vacuum condition to obtain 2.684g of prepolymer, the conversion rate is 90%. UR-IR analysis proves that it contains vinyl acetate and methyl methacrylate blocks, therefore the product is PVAc-b-PMMA block copolymer, GPC gel

chromatography is used to obtain Mn=15600, the molecular weight distribution coefficient Mw/Mn=1.20.

Implementation Example 5

Inside a reaction bottle equipped with condenser, agitator, and nitrogen pipe, 45ml refined VAc monomer is added with 1ml carbon tetrachloride and 0.0500g AIBN, N_2 is sent into the bottle to exchange air for 15 minutes, after agitation, the temperature is raised to 60°C, the reaction proceeds for 120 minutes while the temperature is maintained, then the mixture is cooled to room temperature, 40ml methanol is added, after agitation, the mixture is slowly poured into 200ml petroleum ether, after precipitation, the material is washed by petroleum ether, the treatment is repeated for 3 times, 26g of prepolymer is obtained after first being dried for 2 hours under 50°C and then being dried for 8 hours at 50°C vacuum condition. GPC gel chromatography is used to obtain Mn=58700, measure 3.110g of prepolymer, 0.0051g of cuprous chloride and 0.0254g of 2,2-dipyridyl in the reactor, 5ml styrene and 5ml dimethyl benzene are injected by an injector, the prepolymer is fully dissolved after agitation, nitrogen is used for 3 times to vacuum the reactor at -20°C, the reactor is sealed, and the reaction proceeds for 19 hours at 130°C, the product is dissolved by tetrahydrogen furan and precipitated for 3 times with methanol, the precipitated material is dried for 2 hours at 50°C, than dried for 8 hours under 50°C vacuum condition to obtain 4.33g of prepolymer, the conversion rate is 30%. UR-IR analysis proves that it contains vinyl acetate and styrene blocks, therefore the product is PVAc-b-PSt block copolymer, GPC gel chromatography is used to obtain Mn=81200, the molecular weight distribution coefficient Mw/Mn=1.54.